

## Supplementary Information

### **Development of a Robust Tool to Extract Mulliken and Löwdin Charges from Plane Waves and its Application to Solid-State Materials**

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**Table S1.** Mulliken and Löwdin charges of [NaCl] and [CsCl] type alkaline halides compared with Bader charges and charges expected from the Zintl concept. All charges in units of  $e$ .

Compound	Element	Zintl	Mulliken charge	Löwdin charge	Bader charge
NaF	Na	+1	+0.81	+0.77	+0.85
	F	-1	-0.81	-0.77	-0.85
NaCl	Na	+1	+0.78	+0.67	+0.86
	Cl	-1	-0.78	-0.67	-0.86
NaBr	Na	+1	+0.78	+0.65	+0.86
	Br	-1	-0.78	-0.65	-0.86
NaI	Na	+1	+0.77	+0.61	+0.85
	I	-1	-0.77	-0.61	-0.85
KF	K	+1	+0.81	+0.82	+0.85
	F	-1	-0.81	-0.82	-0.85
KCl	K	+1	+0.79	+0.73	+0.82
	Cl	-1	-0.79	-0.73	-0.82
KBr	K	+1	+0.80	+0.71	+0.82
	Br	-1	-0.80	-0.71	-0.82
KI	K	+1	+0.80	+0.67	+0.81
	I	-1	-0.80	-0.67	-0.81
CsF	Cs	+1	+0.87	+0.87	+0.91
	F	-1	-0.87	-0.87	-0.91
CsCl	Cs	+1	+0.81	+0.78	+0.84
	Cl	-1	-0.81	-0.78	-0.84
CsBr	Cs	+1	+0.82	+0.76	+0.82
	Br	-1	-0.82	-0.76	-0.82
CsI	Cs	+1	+0.81	+0.71	+0.80
	I	-1	-0.81	-0.71	-0.80

**Table S2.** Mulliken, Löwdin, and Bader charges of archetypal Zintl phases in comparison with charges expected from the Zintl concept. All charges in units of  $e$ .

Compound	Unit	Zintl	Mulliken charge	Löwdin charge	Bader charge
LiAl	Li	+1	+0.50	+0.60	+0.83
	Al	-1	-0.50	-0.60	-0.83*
LiTl	Li	+1	+0.39	+0.60	+0.85
	Tl	-1	-0.39	-0.60	-0.85
NaTl	Na	+1	+0.81	+0.67	+0.73
	Tl	-1	-0.81	-0.67	-0.73
KTl	K	+1	+0.67*	+0.63*	+0.66*
	Tl	-1	-0.67*	-0.63*	-0.66*
CsTe <sub>4</sub>	Cs	+1	+0.84	+0.66	+0.78
	Te <sub>4</sub> unit	-1	-0.83	-0.65	-0.78
Cs <sub>2</sub> Te <sub>5</sub>	Cs	+1	+0.83*	+0.68*	+0.76*
	Te <sub>5</sub> unit	-2	-1.67	-1.36	-1.51
Cs <sub>2</sub> I <sub>8</sub>	Cs	+1	+0.90	+0.70	+0.85
	I <sub>8</sub> unit	-2	-1.82	-1.40	-1.69
CaSi	Ca	+2	+1.41	+1.39	+1.26
	Si	-2	-1.41	-1.39	-1.26
	S <sub>8</sub> unit	+2	+1.91	+1.93	+1.89
S <sub>8</sub> (AsF <sub>6</sub> ) <sub>2</sub>	As	+5	+2.57	+2.22	+2.91
	F	-1	-0.59	-0.54	-0.64
	Te <sub>6</sub> unit	+4	+3.48	+3.48	+3.70
Te <sub>6</sub> (As(V)F <sub>6</sub> ) <sub>4</sub> · 2As(III)F <sub>3</sub>	As	+5/+3	+2.58/+1.72	+2.22/+1.49	+2.91/+1.94
	F	-1	-0.57*	-0.51*	-0.64*

\*averaged values

**Table S3.** Mulliken and Löwdin charges of the Zintl phase Sr<sub>14</sub>(Al<sub>4</sub>)<sub>2</sub>(Ge)<sub>3</sub> and NFAl<sub>2</sub>Ca<sub>6</sub> in comparison with Zintl and Bader charges. All charges in units of  $e$ .

Compound	Element	Zintl	Mulliken charge	Löwdin charge	Bader charge
Sr <sub>14</sub> (Al <sub>4</sub> ) <sub>2</sub> (Ge) <sub>3</sub>	Sr	+2	+1.23*	+1.31*	† (+1.13 to +1.20 <sup>1</sup> )
	Al	-2	-1.33*	-1.40*	† (-1.7 <sup>1</sup> )
	Ge	-4	-2.23	-2.40	† (-2.2 <sup>1</sup> )
NFAl <sub>2</sub> Ca <sub>6</sub>	N		-2.25	-2.34	-1.95 (-2.00 <sup>2</sup> )
	F		-0.81	-0.83	-0.92 (-0.98 <sup>2</sup> )
	Al		-2.53	-2.55	-2.27 (-2.13 <sup>2</sup> )
	Ca		+1.35	+1.38	+1.24 (+1.20 <sup>2</sup> )

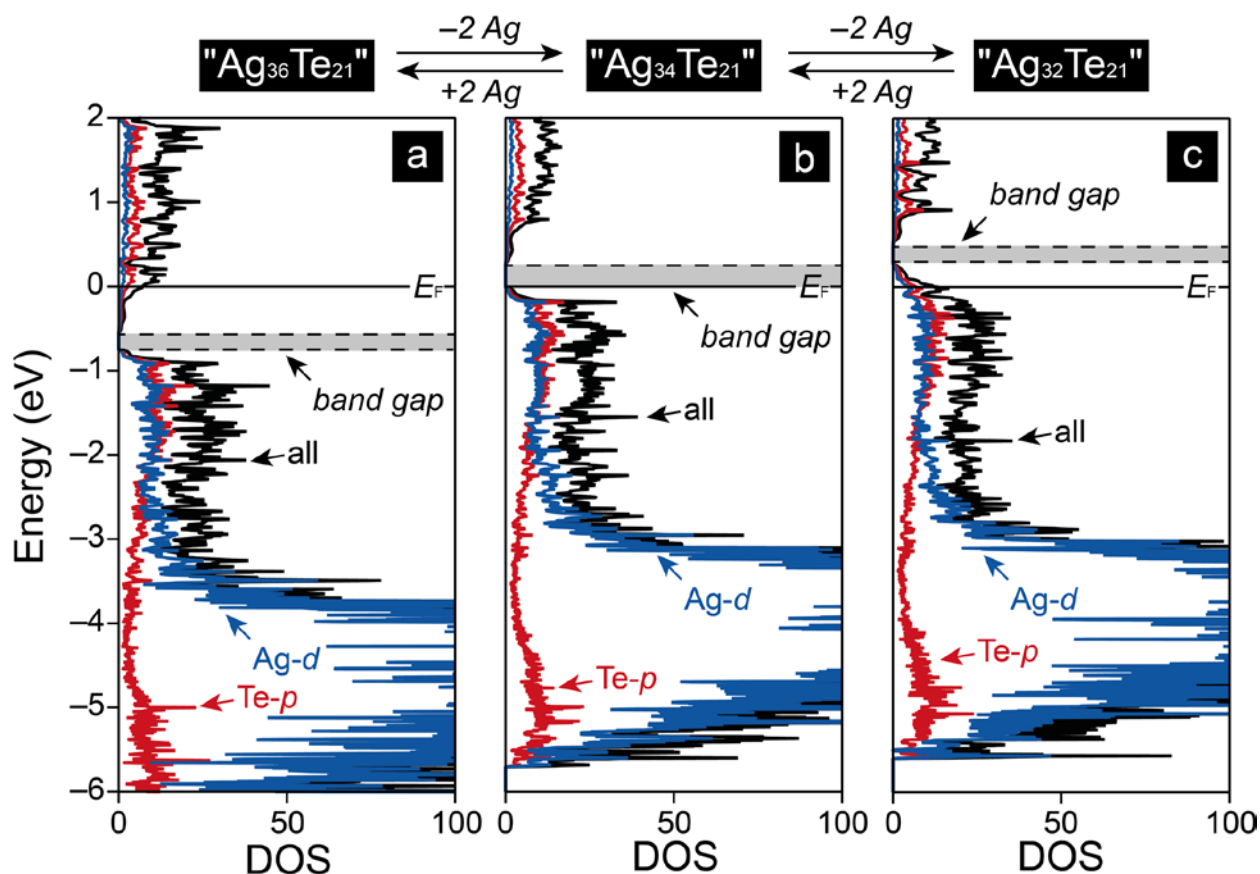
\*averaged values

† calculation still unfinished after more than 23.300 core hours (values in brackets are taken from the literature)

**Table S4.** Mulliken and Löwdin charges of the computational models of stützite. All charges in units of  $e$ .

Compound	Element	Zintl	Mulliken charge	Löwdin charge
"Ag <sub>32</sub> Te <sub>21</sub> "	Ag		+0.26 to +0.43 (+0.37*)	+0.27 to +0.37 (+0.35*)
	Te		-0.56 to -0.78/ -0.38 to -0.41 (-0.66*/-0.40*)	-0.54 to -0.73/ -0.34 to -0.37 (-0.63*/-0.36*)
"Ag <sub>34</sub> Te <sub>21</sub> "	Ag	(Ag <sup>+</sup> ) <sub>34</sub>	+0.27 to +0.42 (+0.36*)	+0.28 to +0.36 (+0.34*)
	Te	(Te <sup>2-</sup> ) <sub>13</sub> ([Te <sup>-</sup> ] <sub>2</sub> ) <sub>4</sub>	-0.58 to -0.74/ -0.39 to -0.42 (-0.68*/-0.36*)	-0.55 to -0.71/ -0.35 to -0.39 (-0.65*/-0.33*)
"Ag <sub>36</sub> Te <sub>21</sub> "	Ag	(Ag <sup>+</sup> ) <sub>36</sub>	+0.26 to +0.42 (+0.33*)	+0.27 to +0.35 (+0.31*)
	Te	(Te <sup>2-</sup> ) <sub>13</sub> ([Te <sup>-</sup> ] <sub>2</sub> ) <sub>4</sub> (e <sup>-</sup> ) <sub>2</sub>	-0.59 to -0.69/-0.42 (-0.64*/-0.42)	-0.57 to -0.67/ -0.39 to -0.40 (-0.63*/-0.39*)

\*averaged values

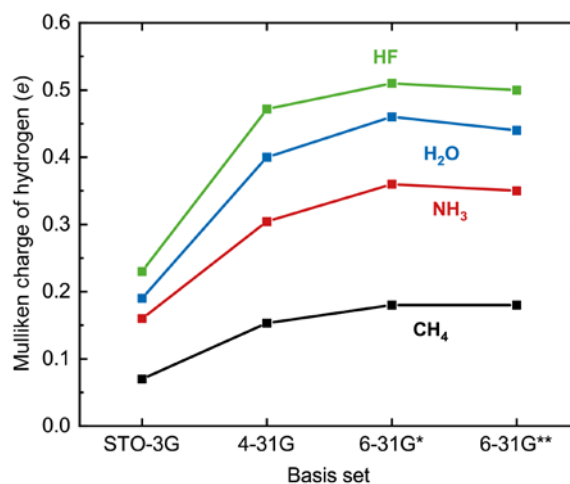


**Figure S1.** Density of states (DOS) of the three models of stützite "Ag<sub>32</sub>Te<sub>21</sub>" (a), "Ag<sub>34</sub>Te<sub>21</sub>" (b), and "Ag<sub>36</sub>Te<sub>21</sub>" (c).<sup>3</sup> Adapted with permission from Ref. 3. Copyright (2018) American Chemical Society.

**Table S5.** Mulliken charges on the hydrogens of a ten-electron series (CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HF). Comparison between results from the literature<sup>4</sup> and LOBSTER as well as Gaussian<sup>5</sup>. All charges in units of *e*.

Compound	Basis set/method	Mulliken charge on hydrogen obtained from a) or b)	Mulliken charge on hydrogen calculated with Gaussian <sup>5</sup>
CH <sub>4</sub>	STO-3G	0.06 <sup>a)</sup>	0.07
	4-31G	0.15 <sup>a)</sup>	0.15
	6-31G*	0.16 <sup>a)</sup>	0.18
	6-31G**	0.12 <sup>a)</sup>	0.18
	LDA	0.23 <sup>b)</sup>	0.22
NH <sub>3</sub>	STO-3G	0.16 <sup>a)</sup>	0.16
	4-31G	0.30 <sup>a)</sup>	0.30
	6-31G*	0.33 <sup>a)</sup>	0.36
	6-31G**	0.26 <sup>a)</sup>	0.35
	LDA	0.36 <sup>b)</sup>	0.36
H <sub>2</sub> O	STO-3G	0.18 <sup>a)</sup>	0.19
	4-31G	0.39 <sup>a)</sup>	0.40
	6-31G*	0.43 <sup>a)</sup>	0.46
	6-31G**	0.34 <sup>a)</sup>	0.44
	LDA	0.41 <sup>b)</sup>	0.44
HF	STO-3G	0.21 <sup>a)</sup>	0.23
	4-31G	0.48 <sup>a)</sup>	0.47
	6-31G*	0.52 <sup>a)</sup>	0.51
	6-31G**	0.40 <sup>a)</sup>	0.50
	LDA	0.65 <sup>b)</sup>	0.49

- a) Values taken from A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry - Introduction to Advanced Electronic Structure Theory*, Dover Publications, Inc.: Mineola, New York, 1996 (Ref. <sup>4</sup>)  
b) As calculated with LOBSTER.



**Figure S2.** Mulliken charges for the ten-electron series (CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HF) as obtained from Hartree–Fock calculations using Gaussian<sup>5</sup>.

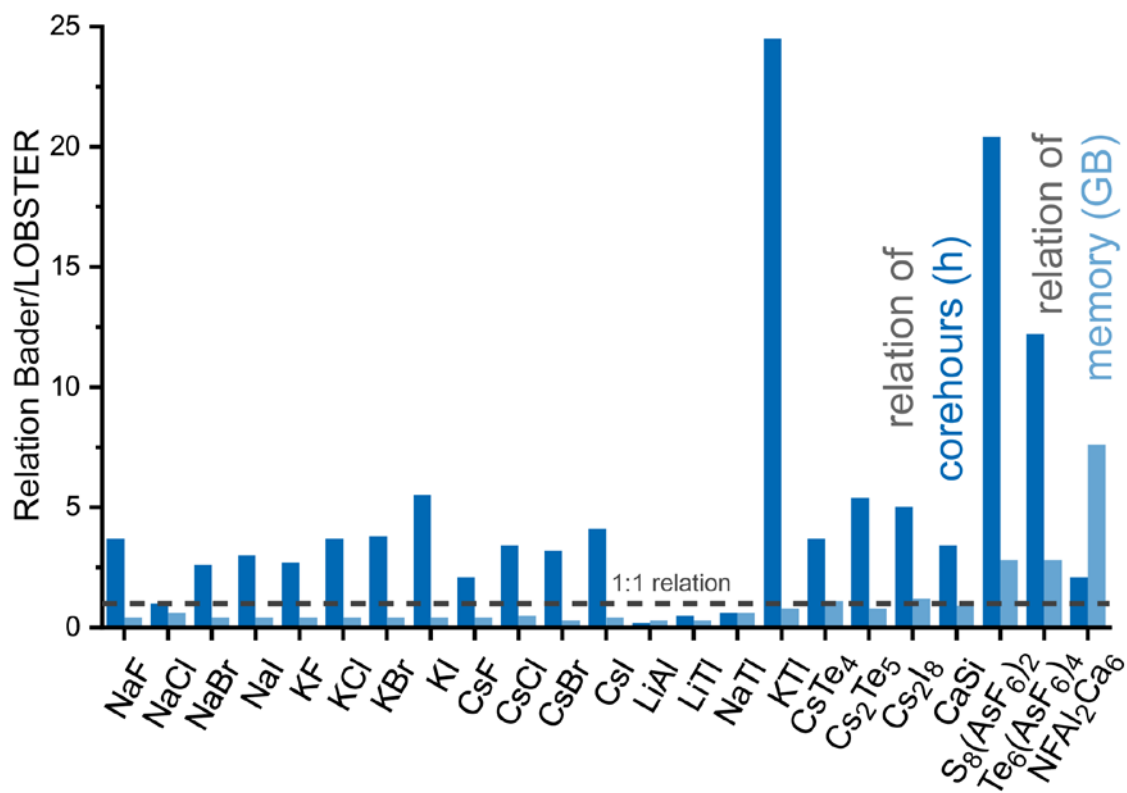
**Table S6.** Lattice parameters and **k**-point mesh for every compound presented in this work.

Compound	Experimental lattice parameter ( <i>a</i> , <i>b</i> , <i>c</i> /Å)	Calculated lattice parameter ( <i>a</i> , <i>b</i> , <i>c</i> /Å)	<b>k</b> -point mesh
NaF	4.6354(6) <sup>6</sup>	4.68	13×13×13
NaCl	5.6573(7) <sup>7</sup>	5.69	11×11×11
NaBr	5.9738(7) <sup>8</sup>	6.04	11×11×11
NaI	6.479 <sup>9</sup>	6.54	11×11×11
KF	5.367(10) <sup>10</sup>	5.41	11×11×11
KCl	6.2849(5) <sup>7</sup>	6.38	11×11×11
KBr	6.5847(7) <sup>11</sup>	6.71	11×11×11
KI	7.0491(7) <sup>11</sup>	7.19	9×9×9
CsF	6.03 <sup>12</sup>	6.11	11×11×11
CsCl	4.126 <sup>13</sup>	4.21	15×15×15
CsBr	4.296992(9) <sup>14</sup>	4.39	13×13×13
CsI	4.56772(2) <sup>15</sup>	4.67	13×13×13
LiAl	6.3667(5) <sup>16</sup>	6.35	9×9×9
LiTl	3.438(2) <sup>17</sup>	3.48	17×17×17
NaTl	7.488(3) <sup>18</sup>	7.67	9×9×9
KTl	15.329(4), 15.069(4), 8.137(2) <sup>19</sup>	15.99, 15.69, 8.10	3×3×7
CsTe <sub>4</sub>	7.857(1), 7.286(1), 14.155(2) <sup>20</sup>	8.16, 7.36, 14.30	7×9×5
Cs <sub>2</sub> Te <sub>5</sub>	9.373(3), 12.288(2), 10.140(2) <sup>21</sup>	9.71, 12.34, 10.34	7×5×5
Cs <sub>2</sub> I <sub>8</sub>	11.19(5), 9.00(4), 10.23(5) <sup>22</sup>	11.67, 9.17, 10.76	5×7×5
CaSi	4.5516(2), 10.7002(4), 3.8869(1) <sup>23</sup>	4.54, 10.76, 3.90	13×5×15
S <sub>8</sub> (AsF <sub>6</sub> ) <sub>2</sub>	15.005(5), 13.401(5), 16.489(5) <sup>24</sup>	15.58, 13.67, 16.57	5×5×3
Te <sub>6</sub> (As(V)F <sub>6</sub> ) <sub>4</sub> · 2As(III)F <sub>3</sub>	14.832, 12.242, 15.301 <sup>25</sup>	15.35, 12.60, 15.63	5×5×5
Sr <sub>14</sub> (Al <sub>4</sub> ) <sub>2</sub> (Ge) <sub>3</sub>	11.9658(2), 11.9658(2), 40.1033(7) <sup>1</sup>	12.00, 12.00, 40.09	7×7×3
NFA <sub>12</sub> Ca <sub>6</sub>	9.85540512 or 6.96882379 (primitive cell) <sup>2</sup>	6.97 (primitive cell) 13.57, 13.55, 8.40 (Ag <sub>32</sub> Te <sub>21</sub> )	10×10×10
Ag <sub>5-x</sub> Te <sub>3</sub>	13.4761(11), 13.4761(11), 8.4769(7) <sup>3</sup>	13.65, 13.65, 8.53 (Ag <sub>34</sub> Te <sub>21</sub> ) 13.81, 13.81, 8.51 (Ag <sub>36</sub> Te <sub>21</sub> )	5×5×7

**Table S7.** Comparison of core hours (h) and resource consumption (memory usage in GB) between the calculation of charges with Bader (B) and LOBSTER (L). Memory only refers to the memory usage of the VASP calculation.

Compound	B (h)	L (h)	Ratio B/L	B (GB)	L (GB)	Ratio B/L
NaF	14.2	3.9	3.7	0.23	0.63	0.4
NaCl	10.8	11.3	1.0	0.24	0.43	0.6
NaBr	14.6	5.6	2.6	0.34	0.87	0.4
NaI	18.3	6.0	3.0	0.41	1.04	0.4
KF	10.8	4.0	2.7	0.26	0.69	0.4
KCl	23.9	6.5	3.7	0.39	0.99	0.4
KBr	30.9	8.2	3.8	0.44	1.12	0.4
KI	27.3	4.9	5.5	0.35	0.81	0.4
CsF	14.2	6.8	2.1	0.35	0.92	0.4
CsCl	3.9	1.1	3.4	0.23	0.43	0.5
CsBr	2.6	0.8	3.2	0.19	0.58	0.3
CsI	3.9	1.0	4.1	0.22	0.63	0.4
LiAl	10.0	47.2	0.2	0.21	0.68	0.3
LiTl	1.3	2.5	0.5	0.25	0.91	0.3
NaTl	89.4	144.9	0.6	0.54	0.97	0.6
KTl	796.6	32.6	24.5	1.19	1.51	0.8
CsTe <sub>4</sub>	95.9	25.6	3.7	1.27	1.12	1.1
Cs <sub>2</sub> Te <sub>5</sub>	154.9	28.5	5.4	0.93	1.13	0.8
Cs <sub>2</sub> I <sub>8</sub>	102.8	20.7	5.0	0.99	0.84	1.2
CaSi	15.7	4.6	3.4	0.62	0.70	0.9
S <sub>8</sub> (AsF <sub>6</sub> ) <sub>2</sub>	14220.1	697.1	20.4	3.99	1.42	2.8
Te <sub>6</sub> (As(V)F <sub>6</sub> ) <sub>4</sub> · 2As(III)F <sub>3</sub>	14246.4	1163.7	12.2	7.23	2.57	2.8
Sr <sub>14</sub> (Al <sub>4</sub> ) <sub>2</sub> (Ge) <sub>3</sub>	†	8454.9	–	†	5.59	–
NFAI <sub>2</sub> Ca <sub>6</sub>	102.3	49.5	2.1	4.23	0.56	7.6
average			5.1			1.1

† calculation still unfinished after more than 23.300 core hours



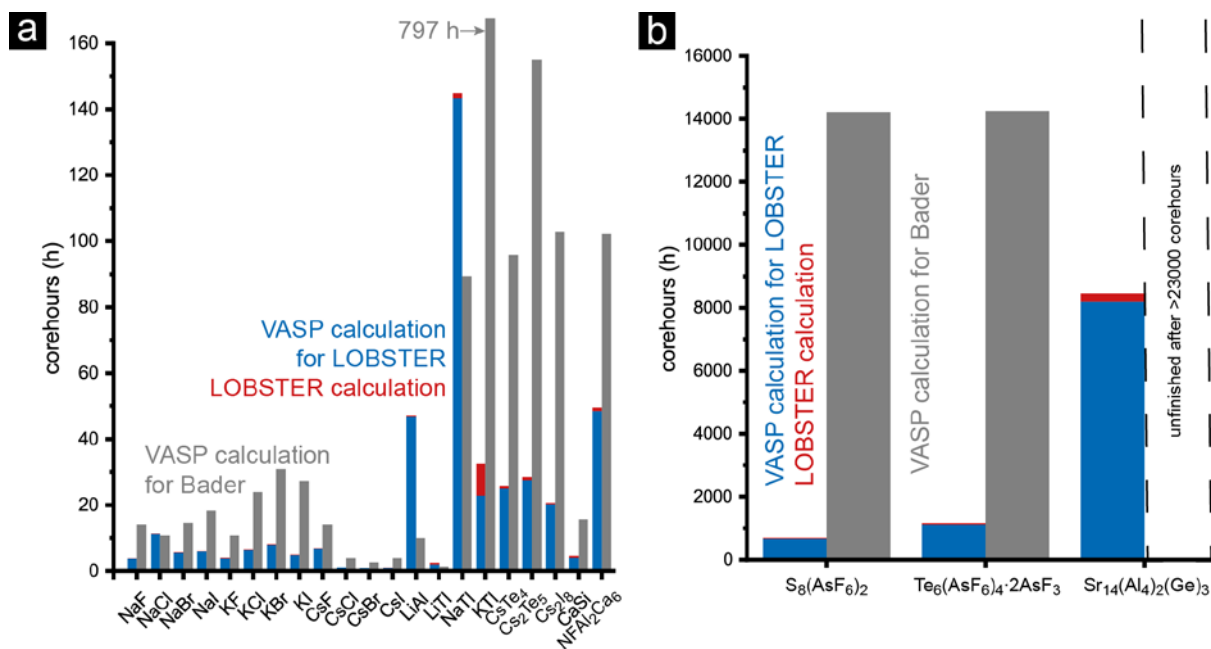
**Figure S3.** Graphical representation of the relation of time and memory consumption of the Bader versus LOBSTER calculations (values correspond to the “ratio” columns in Tab. S7).



**Table S8.** Detailed listing of the number of core hours for LOBSTER and Bader calculations as required by VASP; because the Bader calculations themselves never took longer than 5 s, this time has been safely neglected in the computation time.

Compound	VASP comp. time for LOBSTER (h)	LOBSTER comp. time (h)	VASP comp. time for Bader (h)
NaF	3.8	0.1	14.2
NaCl	11.3	0.1	10.8
NaBr	5.5	0.1	14.6
NaI	5.8	0.1	18.3
KF	3.9	0.1	10.8
KCl	6.4	0.2	23.9
KBr	8.0	0.2	30.9
KI	4.8	0.1	27.3
CsF	6.7	0.1	14.2
CsCl	1.1	0.04	3.9
CsBr	0.8	0.03	2.6
CsI	0.9	0.03	3.9
LiAl	46.8	0.3	10.0
LiTl	2.0	0.5	1.3
NaTl	143.3	1.7	89.4
KTl	22.8	9.7	796.6
CsTe <sub>4</sub>	24.9	0.7	95.9
Cs <sub>2</sub> Te <sub>5</sub>	27.5	1.0	154.9
Cs <sub>2</sub> I <sub>8</sub>	20.3	0.4	102.8
CaSi	4.0	0.6	15.7
S <sub>8</sub> (AsF <sub>6</sub> ) <sub>2</sub>	670.8	26.2	14220.1
Te <sub>6</sub> (As(V)F <sub>6</sub> ) <sub>4</sub>	1125.1	38.7	14246.4
2As(III)F <sub>3</sub>			
Sr <sub>14</sub> (Al <sub>4</sub> ) <sub>2</sub> (Ge) <sub>3</sub>	8192.0	262.9	†
NFAI <sub>2</sub> Ca <sub>6</sub>	48.4	1.0	102.3

† calculation still unfinished after more than 23.300 core hours



**Figure S4.** Graphical representation of the comparison of core hours for Bader versus LOBSTER calculations showing a) simple and b) complex examples.

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